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(54) Title: BIAXIALLY-ORIENTED POLYPROPYLENE FILM CONTAINING PARTICLES OF METAL OR METAL OXIDE			
(57) Abstract A composite film useful for packaging applications is formed from a biaxially-oriented polypropylene base layer having at least one vacuum-coatable polymer outer layer disposed thereon, wherein at least one layer of the composite film contains particles of at least one metal or metal oxide.			

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**BIAXIALLY-ORIENTED POLYPROPYLENE FILM
CONTAINING PARTICLES OF METAL OR METAL OXIDE**

BACKGROUND OF THE INVENTION

Field of the Invention

5 The invention relates to a vacuum-coatable, multi-layered, stretched, heat-sealable polypropylene film having effective barrier properties against water vapor, oxygen, and aromas. The inventive film includes a base layer of polypropylene and at least one additional layer of a polymer, any of which contains particles of metal or metal oxide.

10 **Related Technology**

By virtue of their effective barrier properties against water vapor, oxygen, light and aromas, polypropylene films vacuum coated with metals or metal oxides are usually employed for the packaging of sensitive foodstuffs. Apart from these functional properties, the visual appearance of the film also plays a very important role. Also, the film must be capable of being processed in high-speed packaging machines without difficulty.

15 Due to the need for flexibility in vacuum-coated polypropylene films, a very high affinity of the metal or metal oxide for the surface of the film is important. This generally requires corona or flame pretreatment of the film surface. The barrier properties against water vapor, oxygen, and aromas also critically depend on the material used for, and the composition of, the outer layer on which the metal or metal oxide is deposited.

20 EP-A 329336 describes a coatable film in which the adhesion of the deposited layer is not sufficient for present-day requirements due to the high homopolymer content of the layer to be coated.

EP-A 395204 describes a coatable film which has improved metal adhesion but which has disadvantages as far as its visual appearance is concerned due to the coextrusion process used therein.

EP-A 562496 describes a film containing an ethylene/octene

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copolymer in its outer layer(s); this film, however, is not suitable for vacuum coating due to its shrinkage properties.

The barrier properties of the coated film against water vapor, oxygen, and aromas must be as effective as possible for sophisticated packaging applications.

5 The need has therefore arisen of producing a vacuum-coatable BOPP (biaxially-oriented polypropylene) film which displays excellent adhesion between the metal or the metal oxide and the substrate surface to be coated, and which has a considerably greater barrier effect against water vapor,
10 oxygen, and aromas.

SUMMARY OF THE INVENTION

It is an objective of the invention to overcome one or more of the problems described above.

According to the invention, a vacuum-coatable composite film
15 includes a base layer of biaxially-stretched polypropylene and an additional polymer layer disposed on at least one side of the base layer. At least one of the base layer and the additional layer(s) contains particles of at least one metal or metal oxide.

The inventive film provides an effective barrier against water vapor,
20 oxygen, and aromas.

Other objectives and advantages of the invention may be apparent to those skilled in the art from a review of the following detailed description, taken in conjunction with the appended claims.

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DETAILED DESCRIPTION OF THE INVENTION

The invention provides a biaxially-stretched composite film comprising

- A) a polypropylene base layer and
- 5 B) an outer polymer layer which is disposed on at least one side of the base layer A, wherein either or both layer A and layer B contain particles of at least one metal or metal oxide.

Preferably, a biaxially-stretched, heat-sealable polypropylene film which has been produced by a sequential process has a vacuum-coatable
10 outer layer comprising a polymer containing metallic particles.

Highly preferably, the composite film is heat-sealable. The layer B may be a heat-sealable polymer layer, or an additional, heat-sealable layer C may be disposed on the side of the base layer A opposite layer B. Any of the three layers A, B, and C may contain particles of metal or metal oxide.

- 15 The base layer A may be a polypropylene monolayer or may comprise a multilayer structure including a layer of a polypropylene with a tie layer on one or both sides of the polypropylene layer. The term "polypropylene" as used herein with reference to the base layer generically denotes a semi-crystalline polymer with a majority of polymerized
- 20 propylene, and specifically includes isotactic homopolymers of propylene, copolymers of propylene with up to about 25 mole percent ethylene or butene, terpolymers of propylene with ethylene and butene, and mixtures thereof. The tie layer(s) may comprise modified polyolefins, with preferred polyolefins being those with carboxylic acid or carboxylic acid anhydride
- 25 groups, such as, for example, polypropylene or polyethylene, containing at least one grafted monomer selected from the group consisting of α , β -monounsaturated dicarboxylic acids, such as for example maleic acid, or acid imides thereof, copolymers of ethylene and alpha, beta-monounsaturated carboxylic acids, such as acrylic acid, methylacrylic acid

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and/or the metal (e.g. Zn, Na) salts thereof and/or (C₁-C₄) alkyl esters thereof, or corresponding graft polymers of polyolefins such as polyethylene or polypropylene or known hydrolyzed mixed polymers onto which a monomer of the abovementioned unsaturated acids has been graft-
5 polymerized.

The polymer forming the outer layer can be a polypropylene homo-, co-, or terpolymer, a vinyl alcohol homo- or copolymer, an ethylene/acrylic acid copolymer, a polyamide or copolyamide, or a polyester or copolyester, for example. The outer layer polymer is preferably a polypropylene homo-,
10 co-, or terpolymer.

A tie layer may be disposed on one or both sides of the outer layer when the outer layer polymer is a vinyl alcohol homo- or copolymer, an ethylene/acrylic acid copolymer, a polyamide or copolyamide, or a polyester or copolyester.

The particles of metal or metal oxide are preferably particles of aluminum, oxidized aluminum, or mixtures thereof. The layer(s) A and/or B and/or C contain(s) about 0.1 wt. % to about 5 wt. %, and preferably 0.2 wt. % to about 2 wt. %, of the metal and/or metal oxide, based on the total weight of polymer and metal and/or metal oxide in layer A or layer B. The
20 preferred particle size is between 0.1 μm and 6 μm . The particles can be added to the layer(s) A and/or B and/or C by producing a masterbatch from the particles, in which the metallic particles are dispersed in a polymeric matrix in a comparatively high concentration (e.g., about 1 wt. % to about 10 wt. %, based on the total blend) and the resulting masterbatch is added in
25 a comparatively low concentration (e.g., about 1 wt. % to about 10 wt. % masterbatch based on the layer-forming mixture of polymer and metallic particles) to the polymer used for the production of the layer(s) A and/or B and/or C.

Another method of adding the metal or metal oxide particles to the

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layer(s) A and/or B and/or C comprises the step of regranulating a film which already contains a vacuum-deposited layer of aluminum or aluminum oxide and using this regranulate (or "regrind") in pure form, or in the form of a mixture with a polymer for the production of the layer(s) A, B, or C.

- 5 This process has the advantages that coated film waste can be reused and the metal or metal oxide particles can be distributed very homogeneously in the polymer matrix. A BOPP film which has been coated *in vacuo* with aluminum is preferably used as the film which is regranulated to form the regrind layer.

- 10 In order to improve the adhesion of the particles of metal or metal oxide to the substrate, additives can be added to the layer(s) A and/or B and/or C containing the particles. Such additives preferably comprise modified polyolefins. Preferred modified polyolefins are those with carboxylic acid or carboxylic acid anhydride groups, such as for example polypropylene or polyethylene, containing at least one grafted monomer
15 selected from the group consisting of α,β -monounsaturated dicarboxylic acids, such as for example maleic acid, fumaric acid, itaconic acid, or the acid anhydrides, acid esters, acid amides, or acid imides thereof, copolymers of ethylene and α,β -monounsaturated carboxylic acids, such as acrylic acid,
20 methylacrylic acid and/or the metal (e.g., Zn, Na) salts thereof and/or (C_1 - C_4) alkyl esters thereof, or corresponding graft polymers of polyolefins such as polyethylene or polypropylene or known hydrolyzed mixed polymers onto which a monomer of the abovementioned unsaturated acids has been graft-polymerized.

- 25 Polyolefins such as polypropylene, polyethylene, or copolymers of propylene or ethylene containing a maximum of 1.0 wt. % of a grafted, α,β -monounsaturated dicarboxylic acid anhydride such as maleic anhydride or hydrolyzed mixed polymers thereof are particularly preferred.

Preferably, the base layer A is formed of an isotactic polypropylene

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having a density of about 0.89 g/cm³ to about 0.92 g/cm³ and a melt flow index ("MFI") of about 1 g/10 mins to about 4 g/10 mins at 230°C and a pressure of 21.6 N/cm² (DIN 53 735).

The base layer A preferably contains a heat-sealable layer thereon,
5 which is on the opposite side to the vacuum-coatable layer B.

The following materials are preferably used for the sealable layer:

- random propylene/ethylene copolymers,
- random propylene/1-olefin copolymers,
- random propylene/ethylene/olefin terpolymers, and
- 10 - mixtures of two or three of the abovementioned polymers.

A propylene/ethylene copolymer and a propylene/ethylene/butene
terpolymer are particularly preferred as the heat-sealable layer. The density
of the sealing layer polymers should preferably be in the range from about
0.895 g/cm³ to about 0.960 g/cm³, and the crystalline melting point
15 preferably in the range of about 125°C to about 148°C, depending on the
type of polymer used.

In order to ensure the satisfactory machinability of biaxially-oriented
polypropylene films it is desirable for at least one outer layer to contain
additives such as lubricants and antiblocking agents.

20 Suitable antiblocking agents are inorganic additives such as silicon
dioxide, calcium carbonate, magnesium silicate, aluminum silicate, calcium
phosphate, crosslinked silicone particles, and the like and/or incompatible
organic polymers such as polyamides, polyacrylates, polymethacrylates,
polyesters, polycarbonates, and the like; polymethacrylates and aluminum
25 silicate are preferably used. The effective quantity of antiblocking agent is
in the range from about 0.1 wt. % to about 2 wt. %, and preferably 0.1 wt. %
to about 0.8 wt. %, based on the total layer. The average particle size is
preferably between about 1 μm and about 6 μm, in particular about 2 μm
and about 5 μm, with particles having a spherical shape being particularly

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suitable.

Lubricants include higher aliphatic acid amides, higher aliphatic acid esters, waxes, and metallic soaps, as well as polydimethylsiloxanes. An effective amount of lubricant is typically in the range from about 0.01 wt. % to about 3 wt. %, preferably about 0.02 wt. % to about 1 wt. %, based on the total layer. The addition of polydimethylsiloxanes, and in particular polydimethylsiloxanes having a viscosity of about 5,000 mm²/s to about 1,000,000 mm²/s, in an amount ranging from about 0.02 wt. % to about 2 wt. %, is particularly suitable.

The surface of the polymer layer A or B, whichever is the outer layer can be vacuum coated using any suitable vacuum coating procedure with any suitable metal such as aluminum, zinc, copper, silver, gold, or oxides thereof. The surface of the layer B is preferably vacuum-coated with aluminum, aluminum oxide, or silicon oxide, and particularly preferably with aluminum.

The films according to the invention can be produced by conventional processes such as lamination, coating, interdraw extrusion lamination, or melt coextrusion, using stepwise or non-stepwise procedures, such as interdraw lamination, for example. Generally, the outer polymer layer and the heat-sealable layer will be monoaxially oriented if prepared by lamination, and biaxially oriented if formed by melt coextrusion.

After extrusion and consolidation of the thick film on a casting roller the film is typically stretched in the direction of travel (longitudinally) at a temperature of about 120°C to about 150°C and a stretching ratio of about 4/1 to about 7/1. The stretching ratio in the transverse direction is preferably between about 8/1 and about 12/1 and the transverse stretching of the film is preferably carried out at a temperature between about 130°C and about 170°C. A subsequent annealing step is carried out preferably at about 1°C to about 40°C below the transverse stretching temperature.

EXAMPLES**Example 1**

By means of melt coextrusion a thick film having a layer structure CAB was produced and, after consolidation on a casting roller, was stretched
5 in the direction of travel (longitudinally) at a temperature of 110°C and a stretching ratio of 5/1. Then the film was stretched in the transverse direction at a temperature of 165°C and a stretching ratio of 8.5/1. A subsequent annealing step was carried out at 163°C.

The total thickness of the stretched film was 16 µm.

10 Base layer (A):

Thickness: 14 µm

Material: 100 % of an isotactic polypropylene;
MFI: 1.8 g/10 mins

Outer layer to be vacuum-coated (B):

15 Thickness: 1 µm

Material: 99.5 wt. % of an isotactic polypropylene;
MFI: 1.8 g/10 mins.

20 0.5 wt. % of an aluminum powder (STANDART® Chromal X from Eckart-Werke in Fürth); added in the form of a masterbatch (5 wt. %) using a propylene/ethylene copolymer with an ethylene content of 3.5 mole %.

Sealing layer (C):

25 Thickness: 1 µm

Material: 99.90 % of a propylene/ethylene/butylene terpolymer

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MFI: 8.0 g/10 mins.

0.10% TOSPEARL silicone beads from Toshiba;
average particle size: 2.0 μm .

Example 2

- 5 By means of melt coextrusion a thick film having a layer structure CAB was produced and, after consolidation on a casting roller, was stretched in the direction of travel (longitudinally) at a temperature of 115°C and a stretching quotient of 5/1. Then the film was stretched in the transverse direction at a temperature of 165°C and a stretching ratio of 10/1. A
- 10 subsequent annealing step was carried out at 163°C. The total thickness of the stretched film was 16 μm .

Base layer (A):

- Thickness: 14 μm
- 15 Material: 100% of an isotactic polypropylene; MFI: 3.0 g/10 mins.

Outer layer to be vacuum-coated (B):

- Thickness: 1 μm
- 20 Material: 94.5 wt. % of an isotactic polypropylene; MFI: 3.0 g/10 mins. 5 wt. % of a polypropylene modified with maleic anhydride
- MFI: 5 g/10 mins at 250°C/21.6 N/cm²
- 0.5 wt. % of an aluminum powder (STANDART® Chromal X from Eckart-Werke in Fürth); added in the form of a masterbatch (5 wt. %)

25 **Sealing layer (C):**

Thickness: 1 μm

- 10 -

Material: 99.75 wt. % propylene/ethylene copolymer with an
ethylene content of 3.5 mole %

MFI: 5.0 g/10 mins.

5

0.25 wt. % SiO₂; average particle size: 2.5 μm

Example 3

By means of melt coextrusion a thick film having a layer structure C
CAB was produced, and, after consolidation on a casting roller, was
10 stretched in the direction of travel (longitudinally) at a temperature of 115°C
and a stretching ratio of 5/1. Then the film was stretched in the transverse
direction at a stretching ratio of 10/1 and at a temperature of 165°C. A
subsequent annealing step was carried out at 163°C.

The total thickness of the stretched film was 16 μm.

Base layer (A)

Thickness: 14 μm

Material: 100 % of an isotactic polypropylene

MFI: 3.0 g/10 mins

Outer layer to be vacuum-coated (B):

20 Thickness: 1 μm

Material: 99.5 wt. % of a propylene/ethylene copolymer with an
ethylene content of 3.5 mole %

MFI: 5.0 g/10 mins.

25 0.5 wt. % of an aluminum oxide powder [Admafine®
AO-502 from Admatechs (Toyota)] added in the form
of a masterbatch (5 wt. %)

Sealing layer (C):

Thickness: 1 μm

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Material: 99.75 wt. % of a propylene/ethylene copolymer with an ethylene content of 3.5 mole %

MFI: 5.0 g/10 mins.

0.25 wt. % SiO₂; average particle size: 2.5 μ m

5 Example 4

By means of melt coextrusion a thick film having a layer structure CAB was produced, and, after consolidation on a casting roller, was stretched in the direction of travel (longitudinally) at a temperature of 110°C and a stretching ratio of 5/1. Then the film was stretched in the transverse direction at a temperature of 165°C and a stretching ratio of 8.5/1. A subsequent annealing step was carried out at 163°C.

The total thickness of the stretched film was 16 μ m.

Base layer (A):

Thickness: 14 μ m

15 Material: 100% of an isotactic polypropylene

MFI: 1.8 g/10 mins

Outer layer to be vacuum-coated (B):

Thickness: 1 μ m

20 Material: 100% of a regranulated coated BOPP film (about 0.5 wt. % aluminum/aluminum oxide content)

Sealing layer (C):

Thickness: 1 μ m

Material: 99.90 wt. % of a propylene/ethylene/butylene terpolymer

25

MFI: 8.0 g/10 mins.

0.10 wt. % TOSPEARL silicone beads from Toshiba;
average particle size: 2.0 μm

Example 5

- By means of melt coextrusion a thick film having a layer structure
- 5 CAB was produced, and, after consolidation on a casting roller, was stretched in the direction of travel (longitudinally) at a temperature of 110°C and a stretching ratio of 5/1. Then the film was stretched in the transverse direction at a temperature of 165°C and a stretching ratio of 8.5/1. A subsequent annealing step was carried out at 163°C.
- 10 The total thickness of the stretched film was 16 μm .

Base layer (A):

Thickness: 14 μm
Material: 100% of an isotactic polypropylene
MFI: 1.8 g/10 mins

- 15 **Outer layer to be vacuum-coated (B):**

Thickness: 1 μm
Material: 50 wt. % of a regranulated metallized BOPP film
50 wt. % of an isotactic polypropylene
MFI: 1.8 g/10 mins.

- 20 **Sealing layer (C):**

Thickness: 1 μm
Material: 99.90 wt. % of a propylene/ethylene/butylene terpolymer
MFI: 8.0 g/10 mins.

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0.10 wt. % TOSPEARL silicone beads from Toshiba;
average particle size: 2.0 μm

Example 6 (Comparative Example)

- By means of melt coextrusion a thick film having a layer structure
- 5 AC was produced, and, after consolidation on a casting roller, was stretched in the direction of travel (longitudinally) at a temperature of 110°C and a stretching ratio of 5/1. Then the film was stretched in the transverse direction at a temperature of 165°C and a stretching ratio of 8.5/1. A subsequent annealing step was carried out at 163°C.
- 10 The total thickness of the stretched film was 16 μm .

Base layer (A):

Thickness: 15 μm
Material: 100% of an isotactic polypropylene
MFI: 1.8 g/10 mins

Sealing layer (C):

- Thickness: 1 μm
Material: 99.90 wt. % of a propylene/ethylene/butylene terpolymer
MFI: 8.0 g/10 mins.
- 20 0.10 wt. % TOSPEARL silicone beads from Toshiba;
average particle size: 2.0 μm

Example 7 (Comparative Example)

- By means of melt coextrusion a thick film having a layer structure
- CAB was produced and, after consolidation on a casting roller, was stretched
- 25 in the direction of travel (longitudinally) at a temperature of 110°C and a

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stretching ratio of 5/1. Then the film was stretched in the transverse direction at a temperature of 165°C and a stretching ratio of 10/1. A subsequent annealing step was carried out at 163°C.

The total thickness of the stretched film was 16 μm .

5 Base layer (A):

Thickness: 14 μm

Material: 100% of an isotactic polypropylene; MFI: 1.8 g/10 mins

Outer layer to be vacuum-coated (B):

10 Thickness: 1 μm

Material: 100 wt. % of a propylene/ethylene copolymer with a content of ethylene of 3.5 mole%, MFI: 5.0 g/10 mins.

Sealing layer (C):

15 Thickness: 1 μm

Material: 99.90 wt. % of a propylene/ethylene/butylene terpolymer

MFI: 8.0 g/10 mins.

20 0.10 wt. % TOSPEARL silicone beads from Toshiba;
average particle size: 2.0 μm

The films described in the examples were vacuum-metallized with aluminum until the optical density was about 2.0.

Example 8

By means of melt coextrusion a thick film having layer structure AC
25 was produced and, after consolidation on a casting roller, was stretched in

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the direction of travel (longitudinally) at a temperature of 110°C and a stretching ratio of 5/1. Then the film was stretched in the transverse direction at a temperature of 165°C and a stretching ratio of 8.5/1. A subsequent annealing step was carried out at 163°C.

5 The total thickness of the stretched film was 16 μm .

Base Layer to be vacuum-coated (A):

Thickness: 15 μm

10 Material: 50% of an isotactic polypropylene; MFI: 1.8 g/10 mins
50% of a regranulated metallized BOPP film

Sealing layer (C):

Thickness: 1 μm

15 Material: 99.90 wt. % of a propylene/ethylene/butylene terpolymer
MFI: 8.0 g/10 mins.
0.10 wt. % TOSPEARL silicone beads from Toshiba;
average particle size: 2.0 μm

The following table shows that the films according to the invention were considerably superior to the films not containing any metallic particles.

	WVP (g/m ² d)	O ₂ P (cm ³ /m ² d bar)
Example 1	0.24	67
Example 2	0.23	51
Example 3	0.28	57
Example 4	0.22	48
Example 5	0.10	54
Example 6 (Comparative Example)	0.55	82
Example 7 (Comparative Example)	0.67	93
Example 8	0.15	86

Test methods

10 Determination of water vapor permeability (WVP):

The permeability to water vapor was determined in accordance with DIN 53122, Part 2, at 38°C and a relative difference in atmospheric humidity of 90%.

Determination of oxygen permeability (O₂ P):

15 The permeability to oxygen was determined in accordance with DIN 53380, Part 3, at 23°C and 0% relative atmospheric humidity.

All percentages herein are based on weight unless otherwise indicated.

20 The foregoing detailed description is given for clearness of understanding why, and no unnecessary limitations should be understood therefrom, as modifications within the scope of the invention may become apparent to those skilled in the art.

Claims:

1. A composite barrier film, comprising:
 - (A) a base layer of biaxially-stretched polypropylene, and
 - (B) an outer polymer layer disposed on at least one side of said layer A,wherein at least one of said layer A and said layer B contains particles of at least one metal or metal oxide.
2. A composite film according to claim 1, wherein at least one of said layer A and said layer B comprises a material selected from the group consisting of propylene homopolymers, propylene copolymers, propylene terpolymers, vinyl alcohol homopolymers, copolymers of vinyl alcohols, ethylene/acrylic acid copolymers, polyamides, copolyamides, polyesters, and copolyesters.
3. A composite film according to claim 2, wherein at least one of said layer A and said layer B comprises a propylene homopolymer, propylene copolymer, or propylene terpolymer.
4. A composite film according to claim 1, wherein the particles are selected from the group consisting of aluminum, aluminum oxide, and mixtures of aluminum and aluminum oxide.
5. A composite film according to claim 4, wherein the particles comprise aluminum.
6. A composite film according to claim 1, wherein the size of the particles is between about 0.1 μm and about 6 μm .

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7. A composite film according to claim 1, wherein the particles are added to said layer A or said layer B using a masterbatch comprising the particles in a blend with a polymer in concentration in the range of about 1 wt. % to about 10 wt. %.

5 8. A composite film according to claim 1, wherein the particles are added to said layer A or said layer B by a method in which a film containing a vacuum-deposited layer of aluminum, aluminum oxide, or silicon oxide is regranulated and the resulting regranulate is used in a pure form or in the form of a mixture with polymer to form said layer A or layer
10 B.

9. A composite film according to claim 8, wherein the film containing the vacuum-deposited layer is a BOPP film which has been vacuum-coated with aluminum.

10. A composite film according to claim 1, wherein said layer A
15 or said layer B further contains an additive which improves the adhesion of the particles thereto.

11. A composite film according to claim 10, wherein the additive is selected from the group consisting of

(a) graft copolymers of a polyolefin selected from ethylene
20 homopolymers, ethylene copolymers, propylene homopolymers, and propylene copolymers grafted with a monomer selected from the group consisting of maleic acid, fumaric acid, itaconic acid, maleic anhydride, fumaric anhydride, itaconic anhydride, esters of maleic acid, esters of fumaric acid, esters of itaconic acid, acid amides of maleic acid, acid amides
25 of fumaric acid, acid amides of itaconic acid, imides of maleic acid, imides

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of fumaric acid, and imides of itaconic acid; and,

- (b) ethylene/acrylic acid copolymers, ethylene/methacrylic acid copolymers, metal salts of ethylene/acrylic acid copolymers, metal salts of ethylene/methacrylic acid copolymers, (C₁-C₄) alkyl esters of
5 ethylene/acrylic acid copolymers, (C₁-C₄) alkyl esters of ethylene/methacrylic acid copolymers, graft copolymers of ethylene/acrylic acid copolymers, and graft copolymers of ethylene/methacrylic acid copolymers.

12. A composite film according to claim 1, wherein a heat-
10 sealable layer is disposed on one side of said layer A.

13. A composite film according to claim 12, wherein the heat-sealable layer is a propylene/ethylene copolymer or a propylene/ethylene/butene terpolymer.

14. The composite film according to claim 12 wherein said layer
15 B is a heat-sealable layer.

15. The composite film according to claim 12 wherein said layer B is not heat-sealable and said film comprises a heat-sealable layer disposed on a side of said layer A opposite said layer B.

16. A composite film according to claim 1, wherein at least said
20 layer B contains at least one additive selected from the group consisting of lubricants and antiblocking agents.

17. A composite film according to claim 1, wherein said layer A or said layer B has been subjected to flame, corona, or plasma pretreatment.

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18. A composite film according to claim 1, wherein said layer A or said layer B is vacuum-deposited with a metal or oxide of a metal selected from the group consisting of aluminum, zinc, copper, silver, and gold.

19. A composite film according to claim 1, wherein said layer A
5 or said layer B is vacuum-deposited with aluminum, aluminum oxide, or silicon oxide.

20. A composite film according to claim 19, wherein the vacuum-deposited layer comprises aluminum.

21. A composite film according to claim 1, wherein the film is
10 produced by lamination or melt extrusion.

22. A film according to claim 1, in the form of a single film or as a component of a composite film useful for packaging purposes.

INTERNATIONAL SEARCH REPORT

International Application No

F./US 99/04515

A. CLASSIFICATION / SUBJECT MATTER
 IPC 6 B32B27/28 C08K3/08 C08K3/22 C08J3/22 B29B17/00

According to International Patent Classification (IPC) or to both national classification and IPO

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B C08K C08J B29B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category* Citation of document, with indication, where appropriate, of the relevant passages

Relevant to claim No.

X WO 95 29202 A (BP CHEMICALS PLASTEC GMBH)
 2 November 1995 (1995-11-02)

1-4, 6,
 12-14,
 16, 17,
 21, 22

page 2, paragraph 3
 page 4, last paragraph
 page 5 - page 6
 page 8, paragraph 2
 page 10, last paragraph; claims 7, 9, 20, 21
 abstract

X DE 43 06 123 C (RENKER GMBH & CO. KG.)
 9 June 1994 (1994-06-09)
 column 2, line 7 - line 41
 column 3, line 48 - line 49
 abstract

1, 2, 4-6,
 18-21

-/--

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

30 June 1999

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INTERNATIONAL SEARCH REPORT

International Application No

Pct/US 99/04515

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9536 Derwent Publications Ltd., London, GB; Class A14, AN 95-272979 XP002900519 & JP 07 173311 A (TOYO80 KK), 11 July 1995 (1995-07-11) abstract	1,2,6, 17,21,22
Y	---	8-11
X	DATABASE WPI Section Ch, Week 9423 Derwent Publications Ltd., London, GB; Class A18, AN 94-189094 XP002900520 & JP 06 128433 A (KURARAY CO LTD), 10 May 1994 (1994-05-10) abstract	1,2,16, 21,22
X	---	
X	DATABASE CAPLUS [Online] Document no 121:257466, KURARY CO: "Ethylene-vinyl alcohol copolymer compositions for gas-barrier UV-shield films and laminates" retrieved from STN INTERNATIONAL Database accession no. 1994:657466 XP002900521 abstract & JP 06 128433 A (KURARY CO LTD) 10 May 1994 (1994-05-10)	1,2,16, 21,22
X	---	
X	DATABASE WPI Section Ch, Week 9733 Derwent Publications Ltd., London, GB; Class A60, AN 97-363639 XP002900522 & WO 97 24392 A (TOYO INK MFG CO LTD), 10 July 1997 (1997-07-10) abstract	1,7
Y	---	
Y	EP 0 634 258 A (B.M.P. HOLDING B.V.) 18 January 1995 (1995-01-18) page 2, line 17 - line 28; example 4 abstract	8,9
Y	---	
Y	WO 94 15981 A (NESTE OY) 21 July 1994 (1994-07-21) page 1, line 4 - line 9 page 2, line 16 - line 25; claim 10 abstract	10,11

	-/--	

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/04515

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 810 259 A (BAYER AG.) 3 December 1997 (1997-12-03) page 2, line 17 - page 3, line 7 page 3, line 55 - page 4, line 18 abstract -----</p>	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PLT/US 99/04515

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9529202 A	02-11-1995	DE 4414669 A CA 2186089 A EP 0757703 A HU 75014 A JP 9512292 T NO 964550 A	02-11-1995 02-11-1995 12-02-1997 28-03-1997 09-12-1997 25-10-1996
DE 4306123 C	09-06-1994	CH 686076 A	29-12-1995
JP 7173311 A	11-07-1995	NONE	
JP 6128433 A	10-05-1994	NONE	
JP 06128433 A	10-05-1994	NONE	
WO 9724392 A	10-07-1997	AU 1209397 A	28-07-1997
EP 634258 A	18-01-1995	BE 1007288 A NL 9301760 A	09-05-1995 01-02-1995
WO 9415981 A	21-07-1994	FI 925965 A AT 176792 T AU 679953 B AU 5652694 A DE 69323567 D EP 0729481 A ES 2127374 T JP 8505181 T NO 952590 A US 5698637 A	01-07-1994 15-03-1999 17-07-1997 15-08-1994 25-03-1999 04-09-1996 16-04-1999 04-06-1996 28-06-1995 16-12-1997
EP 810259 A	03-12-1997	DE 19621308 A	04-12-1997